Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Thursday 17 June 2010 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
  – *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
  – *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
  – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Propanone reacts with iodine in acidic solution as shown in the equation below.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The rate equation for the reaction is

$$\text{Rate} = k[CH_3COCH_3(aq)][H^+(aq)]$$

(a) The most appropriate technique to investigate the rate of this reaction is

(1)

☒ **A** titrating samples of reaction mixture with acid.

☒ **B** measurement of optical activity.

☒ **C** measurement of the volume of gas given off.

☒ **D** colorimetry.

(b) Which statement about the reaction is **not** correct?

(1)

☒ **A** The overall order of reaction is second order.

☒ **B** The units of the rate constant are $dm^3\,mol^{-1}\,s^{-1}$.

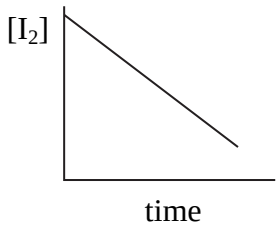
☒ **C** The rate constant increases with temperature.

☒ **D** The rate increases four times when the concentration of propanone and iodine are both doubled.

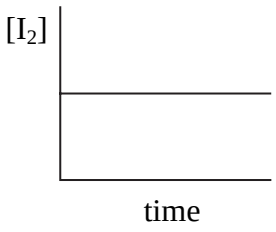
(c) The reaction is carried out using a large excess of both propanone and acid.
Which of the graphs below shows the change of iodine concentration with time?

(1)

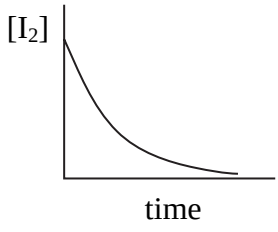
☒ **A**



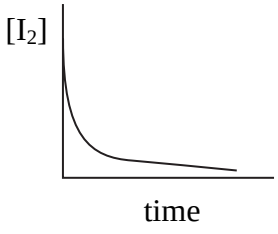
☒ **B**



☒ **C**



☒ **D**



(Total for Question 1 = 3 marks)

2 Which of the following is true for the exothermic reaction shown below?

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

☒ **A**	ΔH	positive
☒ **B**	$\Delta S_{surroundings}$	positive
☒ **C**	ΔS_{system}	negative
☒ **D**	ΔS_{total}	negative

(Total for Question 2 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

3 In which reaction is water acting as a Brønsted-Lowry acid?

☒ **A** $H_2O + HCl \rightarrow H_3O^+ + Cl^-$

☒ **B** $H_2O + SO_3 \rightarrow H_2SO_4$

☒ **C** $H_2O + NH_3 \rightarrow NH_4^+ + OH^-$

☒ **D** $H_2O + CO_2 \rightarrow H_2CO_3$

(Total for Question 3 = 1 mark)

4 Which of the following compounds has both optical and *E*-*Z* isomers?

☒ **A** $CH_3CH{=}CHCH_2CH_3$

☒ **B** $CH_3CHClCH{=}C(CH_3)_2$

☒ **C** $CH_3CCl{=}CClCH_3$

☒ **D** $CH_3CHBrCH{=}CHCl$

(Total for Question 4 = 1 mark)

5 Which of the following reacts with hydrogen cyanide, HCN, to make a racemic mixture?

☒ **A** Methanal, HCHO

☒ **B** Ethanal, CH_3CHO

☒ **C** Propanone, CH_3COCH_3

☒ **D** Pentan-3-one, $C_2H_5COC_2H_5$

(Total for Question 5 = 1 mark)

6 Which of the following is a redox reaction?

☒ **A** Ethanal reacting with Tollens' reagent.

☒ **B** Ethanoyl chloride reacting with ammonia.

☒ **C** Ethanoic acid reacting with ethanol.

☒ **D** Ethanoic acid reacting with sodium hydroxide.

(Total for Question 6 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

7 The following methods can be used to distinguish between pairs of organic compounds without further tests.

A Warm each compound with Fehling's or Benedict's solution.

B Add solid sodium carbonate to each compound.

C Add 2,4-dinitrophenylhydrazine (Brady's reagent) to each compound.

D Add water, drop by drop, to each compound.

(a) Which test would distinguish propanone from propan-1-ol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which test would distinguish between aqueous solutions of ethanoic acid and ethanol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which test would distinguish ethanoyl chloride from ethanol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 7 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

8 When propanone reacts with iodine in the presence of sodium hydroxide, the crystalline solid product has the formula

☒ **A** CH_3I

☒ **B** CHI_3

☒ **C** CH_3COCH_2I

☒ **D** CH_3COCI_3

(Total for Question 8 = 1 mark)

9 When the following reaction mixtures are warmed, which will contain ethanoic acid as one of the products?

☒ **A** Ethyl methanoate and sodium hydroxide solution.

☒ **B** Ethyl methanoate and dilute sulfuric acid.

☒ **C** Methyl ethanoate and sodium hydroxide solution.

☒ **D** Methyl ethanoate and dilute sulfuric acid.

(Total for Question 9 = 1 mark)

10 The spectra of the compounds with the formulae $CH_3CH(OH)CH_3$ and $CH_3CH_2CH_2OH$ can be distinguished by

☒ **A** the value of *m/e* of the molecular ion in the mass spectrum.

☒ **B** the presence of a fragment with *m/e* =15 in the mass spectrum.

☒ **C** the presence of an absorption peak due to O–H in the infrared spectrum.

☒ **D** the number of peaks in the nmr spectrum.

(Total for Question 10 = 1 mark)

11 Which of the following has two singlet peaks in its nmr spectrum?

☒ **A** Methanal, HCHO

☒ **B** Methanol, CH_3OH

☒ **C** Chloromethane, CH_3Cl

☒ **D** Dichloromethane, CH_2Cl_2

(Total for Question 11 = 1 mark)

12 The nmr spectrum of 2,2-dimethylpropane, $H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—CH_3$, contains

- ☒ **A** one singlet peak.
- ☒ **B** four singlet peaks.
- ☒ **C** one quartet peak.
- ☒ **D** four quartet peaks.

(Total for Question 12 = 1 mark)

13 Which of the following solutions has the lowest pH?

- ☒ **A** 0.010 mol dm^{-3} hydrochloric acid.
- ☒ **B** 0.100 mol dm^{-3} hydrochloric acid.
- ☒ **C** 0.010 mol dm^{-3} ethanoic acid.
- ☒ **D** 0.100 mol dm^{-3} ethanoic acid.

(Total for Question 13 = 1 mark)

14 Which of the following solutions, when mixed, would make a buffer with pH more than 7?

- ☒ **A** Methanoic acid and sodium methanoate.
- ☒ **B** Sodium hydroxide and sodium chloride.
- ☒ **C** Ammonia and ammonium chloride.
- ☒ **D** Ammonium chloride and ammonium ethanoate.

(Total for Question 14 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

15 This question is about the equilibrium reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

Which statement is **not** correct?

☒ **A** The units of K_p are atm^{-2}.

☒ **B** K_p increases as temperature is decreased.

☒ **C** K_p increases when the pressure increases.

☒ **D** K_p increases when the total entropy change, ΔS_{total}, increases.

(Total for Question 15 = 1 mark)

16 1,2-dichloroethane decomposes in the presence of a catalyst.

$$CH_2ClCH_2Cl(g) \rightleftharpoons CH_2{=}CHCl(g) + HCl(g) \qquad \Delta H = +51 \text{ kJ mol}^{-1}$$

Which of the following would result in an increase in the equilibrium yield of chloroethene?

☒ **A** Increasing the temperature.

☒ **B** Increasing the pressure.

☒ **C** Increasing the surface area of the catalyst.

☒ **D** Changing the catalyst to a more efficient one.

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

17 A bromoalkane has the molecular formula C_4H_9Br. The ionic equation for the hydrolysis of this compound with aqueous sodium hydroxide is shown below.

$$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$$

(a) The rate of hydrolysis was investigated by mixing a large excess of the bromoalkane with aqueous sodium hydroxide, and measuring the time taken for **all** the hydroxide ions to be used up. This was carried out with different initial concentrations of the bromoalkane and the hydroxide ions. The results are shown in the table below.

Experiment	$[C_4H_9Br]$ /mol dm^{-3}	$[OH^-]$ /mol dm^{-3}	Time for OH^- to be used up/s	Initial rate /mol dm^{-3} s^{-1}
1	0.017	0.0012	42	2.9×10^{-5}
2	0.034	0.0012	21	5.7×10^{-5}
3	0.034	0.0020	35	.....

(i) Complete the missing value of the initial rate in the table.

(1)

(ii) State the order of the reaction with respect to C_4H_9Br and to OH^-. Justify each answer by reference to the concentrations of both reactants.

(3)

Order with respect to C_4H_9Br .....

Reason .....

.....

Order with respect to OH^- .....

Reason .....

.....

(iii) Deduce the rate equation for the reaction.

(1)

Rate = ...

(iv) Use the results for the first experiment in the table to calculate the rate constant and give its units.

(2)

Units .....

(b) What evidence supports the theory that there is more than one step in the reaction mechanism?

(1)

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(c) Write the mechanism for the hydrolysis of C_4H_9Br which is consistent with your rate equation. Show the structure of C_4H_9Br clearly in your mechanism.

(3)

*(d) Explain why primary and tertiary bromoalkanes are hydrolysed by different mechanisms.

(2)

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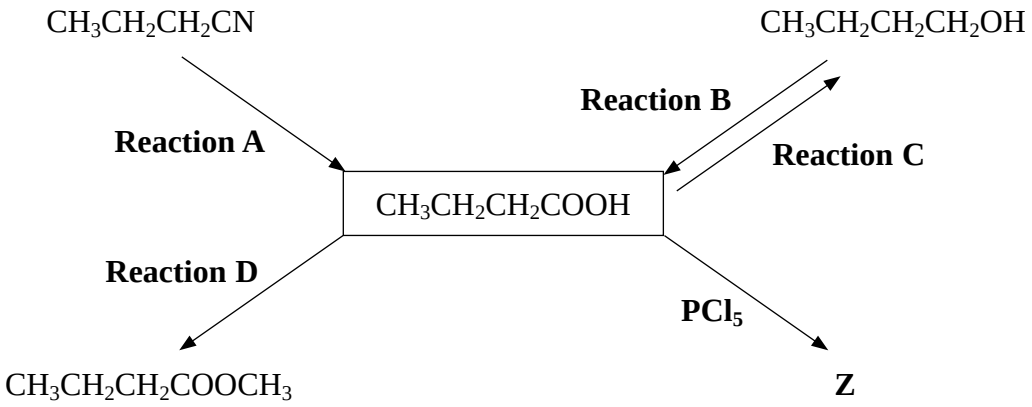
(Total for Question 17 = 13 marks)

18 This question is about butanoic acid, $CH_3CH_2CH_2COOH$.

(a) Some reactions involving butanoic acid are shown below.



(i) What type of reaction is **Reaction A**?

(1)

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(ii) Identify, by name or formula, the reagent which is used with sulfuric acid to carry out **Reaction B**.

(1)

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(iii) What reagent is used in **Reaction C**?

(1)

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(iv) Name the organic product of **Reaction D** and write a balanced equation for its formation.

(2)

Name .....

Equation

(v) Write the **displayed** formula for **Z**, the organic product of the reaction of butanoic acid with phosphorus(V) chloride, PCl_5.

(1)

(b) Butanoic acid and propane-1,2,3-triol are formed when fats in milk are hydrolysed. The presence of milk fat in low fat spreads is detected by hydrolysing the spread, and then analysing the products using gas chromatography (also called gas-liquid chromatography, GLC).

(i) Explain why nitrogen, rather than oxygen, is used as the carrier gas in GLC.

(1)

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(ii) What property determines whether butanoic acid or propane-1,2,3-triol would move faster through the chromatography column?

(1)

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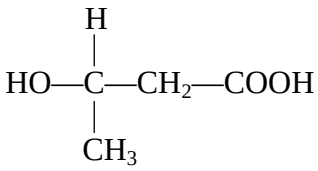
(c) The formula of 3-hydroxybutanoic acid is shown below.



(i) 3-hydroxybutanoic acid can form a polymer which is used to make "green" packaging as it is biodegradable.

Draw a section of this polymer, showing TWO monomer units. Clearly show any double bonds.

(2)

(ii) The polymer cannot be used in acidic conditions. What reaction would occur when the polymer is in prolonged contact with an acid?

(1)

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(Total for Question 18 = 11 marks)

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19 Ethanoic acid can be manufactured by the following reaction, which is carried out between 150 °C and 200 °C.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(a) A mixture of 50.0 mol of methanol and 50.0 mol of carbon monoxide reaches equilibrium at a pressure of 32.0 atm. At 175 °C, the equilibrium partial pressure of ethanoic acid is 22.2 atm.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

(ii) Calculate the partial pressures of methanol and carbon monoxide at equilibrium.

(2)

Methanol .....

Carbon monoxide .....

(iii) Calculate the value of K_p for this reaction at 175 °C. Include a unit in your answer and give your answer to **three** significant figures.

(2)

(b) Another sample of 50.0 mol of methanol and 50.0 mol of carbon monoxide was allowed to reach equilibrium at the same pressure of 32.0 atm, but at a lower temperature. 93.6 % of the methanol was converted at equilibrium.

(i) Complete the table below to show the number of moles of each species in the equilibrium mixture.

(2)

	CH_3OH	CO	CH_3COOH
Number of moles at start	50.0	50.0	0
Number of moles at equilibrium			

(ii) Calculate the partial pressure of ethanoic acid in the equilibrium mixture.

(1)

(iii) Is the reaction exothermic or endothermic? Explain your answer.

(1)

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(c) How, if at all, does the addition of methanol to the equilibrium mixture affect the following? Justify your answers.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(i) The equilibrium constant for the formation of ethanoic acid.

(1)

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(ii) The equilibrium yield of ethanoic acid.

(1)

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(d) In industry, catalysts are used even though they are often expensive.

State and explain ONE benefit to the **environment** resulting from the use of catalysts in industrial processes.

(2)

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(Total for Question 19 = 13 marks)

20 Vinegar is used as a food preservative. It is an acidic solution containing ethanoic acid, CH_3COOH.

(a) A titration was carried out to measure the concentration of ethanoic acid in a sample of vinegar. 25.0 cm^3 of a vinegar solution was titrated with a solution of sodium hydroxide, concentration 0.250 mol dm^{-3}. The concentration of the ethanoic acid in the vinegar solution was found to be 0.125 mol dm^{-3}.

(i) Calculate the pH of 0.250 mol dm^{-3} sodium hydroxide at 298 K.

[$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 298 K.]

(2)

(ii) Write the expression for the acid dissociation constant, K_a, for ethanoic acid.

(1)

(iii) Calculate the pH of 0.125 mol dm^{-3} ethanoic acid at 298 K.

[K_a for ethanoic acid is 1.7×10^{-5} mol dm^{-3} at 298 K.]

(2)

(iv) When half the ethanoic acid is neutralized, the concentration of the remaining ethanoic acid equals the concentration of the sodium ethanoate which has formed. What is the pH of the mixture at this point? Justify your answer.

(2)

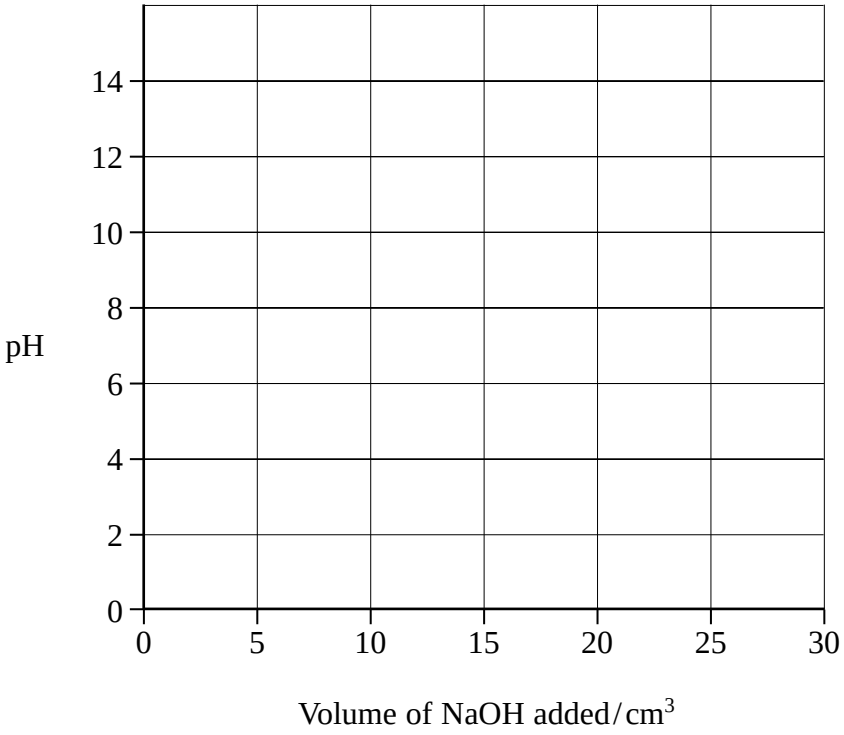
pH .....

Justification .....

.....

(v) On the axes below, sketch the titration curve for this reaction when 30 cm^3 of the sodium hydroxide is added to 25.0 cm^3 of the vinegar solution.

(3)



*(vi) The only indicators which were available for this titration were methyl yellow (in ethanol) and thymolphthalein. Explain which indicator is more suitable for this titration and why the other is unsuitable. You will need to refer to your data booklet.

(2)

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(b) In the food industry, ethanoic acid is described as an acidity regulator, additive number E260.

Ethanoic acid can neutralize alkalis. What substance could be mixed with ethanoic acid so that it regulates pH as a buffer in foodstuffs?

(1)

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(Total for Question 20 = 13 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

21 (a) Crystals of hydrated cobalt(II) chloride, $CoCl_2.6H_2O$, lose water when they are heated, forming anhydrous cobalt(II) chloride, $CoCl_2$.

$$CoCl_2.6H_2O(s) \rightarrow CoCl_2(s) + 6H_2O(l)$$

(i) Calculate the entropy change of the system, $\Delta S^{\ominus}_{system}$, at 298 K. Include a sign and units in your answer. You will need to refer to your data booklet.

(2)

(ii) Explain whether the sign of your answer to (a)(i) is as expected from the equation for the reaction.

(1)

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(iii) The standard enthalpy change for the reaction, $\Delta H^{\ominus}$, is +88.1 kJ mol^{-1}. Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, at 298 K for this reaction. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, at 298 K for the reaction.

(1)

(v) Does your answer to (a)(iv) indicate whether hydrated cobalt(II) chloride can be stored at 298 K without decomposition? Explain your answer.

(1)

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(b) A student attempted to measure the enthalpy change of solution of anhydrous cobalt(II) chloride by adding 2.00 g of cobalt(II) chloride to 50.0 cm^3 of water in a well-insulated container. A temperature rise of 1.5 °C was recorded.

The student used a balance which reads to 0.01g, a 50.0 cm^3 pipette, and a thermometer which can be read to 0.25 °C.

(i) Which measuring instrument should be changed to give a result which is closer to the accepted value? Justify your answer.

(2)

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(ii) Suggest ONE **other** change the student could make to give a result which is closer to the accepted value. Justify your suggestion.

(2)

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*(c) The lattice energies of magnesium chloride, $MgCl_2$, calcium chloride, $CaCl_2$, and strontium chloride, $SrCl_2$ are shown in the table below.

Chloride	Lattice energy/kJ mol^{-1}
$MgCl_2$	–2526
$CaCl_2$	–2258
$SrCl_2$	–2156

(i) Use data on ionic radii, from your data booklet, to explain the trend in these values. Estimate a value for the lattice energy of cobalt(II) chloride, giving ONE piece of data to justify your estimate.

(4)

(ii) Explain how lattice energy values, together with other data, can be used to predict the solubility of ionic compounds.

(3)

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*(d) Cobalt forms another chloride, $CoCl_3$, but scientists predict that $MgCl_3$ cannot be made. Suggest a reason for this.

You should consider the enthalpy changes in the Born-Haber cycle, which provide evidence about why cobalt(III) chloride is known but magnesium(III) chloride is not.

(2)

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(Total for Question 21 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4											10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103